# 14th group Elements

C - $[He]\ 2s^2 2p^2$

GEC = $ns^2np^2$

Si - $[Ne]\ 3s^2 3p^2$

Ge - $[Ar]\ 3d^{10} 4s^2 4p^2$

Sn - $[Kr]\ 4d^{10}\ 5s^2 5p^2$

Pb - $[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^2$

## Occurence

- Si is second most abundant element in earth's crust.
- C is the next most abundant element in 14th group. It is available in both free and combined state.
- Ge is available in trace quantities.
- Sn is available as Casseterite (Tin stone) - $SnO_2$
- Pb is available as Galena (PbS)
  Anglesite ($PbSO_4$)
  Cerrusite ($PbCO_3$)

## General Properties

### 1. Metallic nature

C, Si → Non metals

Ge → Metalloid

Sn, Pb → Metals with low M.P (as only 2 $e^-$ per metal are involved due to inert pair effect)
Metallic bond is weak

- Tin, Lead are easily fusible because the metallic bond is weaker due to the involvement of only 2 valence $e^-$ per metal atom (inert pair effect)

### 2. Covalent Radius: C $\xrightarrow{Inc}$ Pb

C $\xrightarrow[\text{Inc}]{\text{Usual}}$ Si $\xrightarrow{\text{Less inc}}$ Ge $\xrightarrow{\text{Less inc}}$ Sn $\xrightarrow[\text{Ineffective}]{\text{Less inc}}$ Pb

S·E of s & p

Poor S·E of d e⁻

Poor S·E of d e⁻

~~Poor~~ S·E of d f-e⁻ (lanthanide contraction)

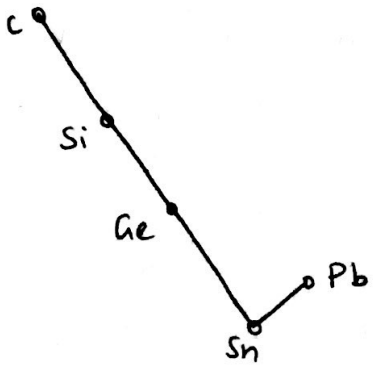
**Ionic radius** : $Si^{4+} \xrightarrow{Inc} Pb^{4+}$

$Si^{2+} \xrightarrow{Inc} Pb^{2+}$

(Carbon doesnt form cation)

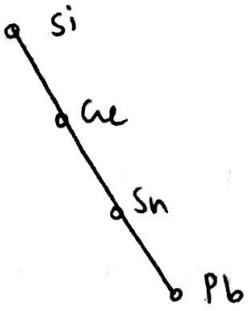
**Density** : C (graphite) < Si < C (diamond) < Ge < Sn < Pb

**MP:**




Sn & Pb have lower MP.

**BP:**




(Carbon undergo sublimation)

**$IP_1$** : C > Si > Ge > **Pb > Sn** (lanthanide contraction)

**$IP_2$**: C > Si > Ge > **Pb > Sn**

**$IP_3$** : C > **Ge > Si** > **Pb > Sn**

**$IP_4$** : C > **Ge > Si** > **Pb > Sn**

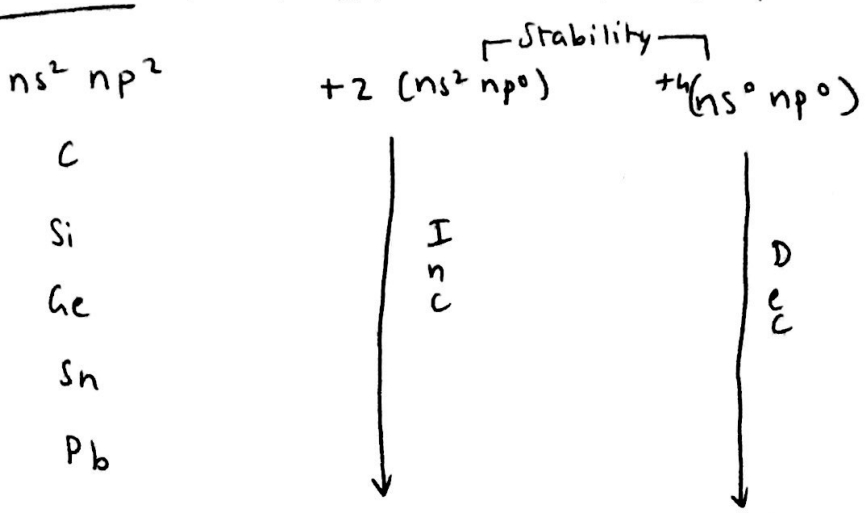
From C to Si, decrease in IP is more and among remaining, it is less due to poor screening effect.

**EN:**

| C | Si | Ge | Sn | Pb |
|---|---|---|---|---|
| 2.5 | 1.8 | 1.8 | 1.8 | 1.9 |

The EN decreases from C to Si. Thereafter, it remains almost constant.

**Oxidation states** : common O.S : $-4, +2, +4$




From C to Pb, the stability of +2 increases while +4 decreases due to increase of inert pair effect.

Stability of: $Si^{2+} < Ge^{2+} < Sn^{2+} < Pb^{2+}$ ($C^{+2}$ isolated ion is not seen but +2 O.S is seen)

Stability of: $Si^{4+} > Ge^{4+} > Sn^{+4} > Pb^{4+}$

Stability of: $Pb^{+2} > Pb^{+4}$ ($PbCl_2 > PbCl_4$) (Prominent inert pair effect)

$Pb^{4+}$ behaves as oxidant

Stability of $Ge^{2+} < Ge^{4+}$

$Sn^{2+} < Sn^{4+}$

- Carbon never forms isolated cation due to higher IP.
- $Sn^{2+}$, $Ge^{2+}$ → reductants

**Catenation power:** $C >> Si > Ge \simeq Sn > Pb$

Catenation power $\propto$ M-M single bond energy

B.E of $C-C > Si-Si > Ge-Ge \geq Sn-Sn > Pb-Pb$

- The element with highest catenation power in the periodic table is carbon.
- On account of highest catenation power, carbon forms chains of infinite length.

## Allotropy :

- All elements exhibit allotropy except Pb.

Allotropes of C: Diamond, Graphite, Fullerenes, Wood charcoal, Animal charcoal, Sugar charcoal, Coconut charcoal, Coal, Coke, Gas Carbon, Petroleum coke

Silicon allotropes: Crystalline, Amorphous

Germanium - 2 crystalline forms

Tin - Grey, white, rhombic forms.

## Covalency

- Max. covalency of C is 4. It cannot extend beyond 4 due to the absence of d-orbitals.
- Other elements exhibit a covalency of 6.

  Ex: $[SiCl_6]^{-}$, $[GeCl_6]^{2-}$ etc.

## Multiple bond formation:

- Carbon forms stronger $p\pi - p\pi$ bonds.

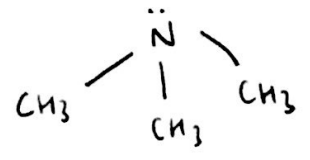
  Reason - Due to the small size, the p-orbitals undergo effective side wise overlap.

  Ex: $>C=C<$ $\quad -C\equiv C- \quad >C=O \quad >C=S \quad -C\equiv N \quad -C=N-$

- Si, Ge, Sn, Pb cannot form effective $p\pi - p\pi$ bonds due to their larger sizes
- C cannot form $d\pi - p\pi$ (→ of C) or $d\pi - d\pi$ bonds due to absence of d-orbitals
- Si, Ge, Sn, Pb can form effective $p\pi - d\pi$ and $d\pi - d\pi$ bonds due to the availability of d-orbitals.

$N(CH_3)_3$

Trimethyl amine



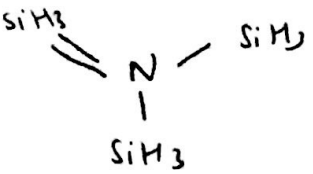
N → sp3

Pyramidal

Bond order = 1 (No resonance)

Lewis basic strength is more

$N(SiH_3)_3$




$N \rightarrow sp^2$

Triangular planar

B.O = $4/3$ = 1.333 (∵ 3 Resonating structure)

Lewis basic strength is very low

## Chemical Properties:

### 1. With air:

Upon heating in air, these elements produce monoxides and dioxides.

| | MO | $MO_2$ |
|---|---|---|
| (unstable at room T exists at higher temp) | CO → neutral | $CO_2$ - Acidic |
| | SiO → neutral | $SiO_2$ - Acidic |
| | GeO → Acidic | $GeO_2$ - Acidic |
| | SnO, PbO → Amphoteric | $SnO_2$ - Amphoteric |
| | | $PbO_2$ - Amphoteric |

**CO**

- $:C:\overset{\curvearrowleft}{\underset{\times}{\overset{\times}{O}}}\overset{\times}{\times} \equiv :C \overset{\leftarrow}{\equiv} O\overset{\times}{\times}$ Bond order = 3 $(:\overset{\ominus}{C} \equiv \overset{\oplus}{O}\overset{\times}{\times})$

Because of the ~~bond~~ back bond formation, the dipole moment of CO is much less than the expected value.

- Amongst diatomic molecules, CO possesses the highest bond energy.
- CO acts as monodented ligand (can donate only one pair of $e^-$) and also as bridged ligand ($-\overset{\overset{O}{\|}}{C}-$)

While acting as ligand, C donates the lone pair due to its lesser EN.

- In metal carbonyls, CO involves in synergic bonding which is formed by the overlapping of filled d-orbital of metal with the vacant $\pi^*$ orbital of CO. (Chem bonding · MOT)

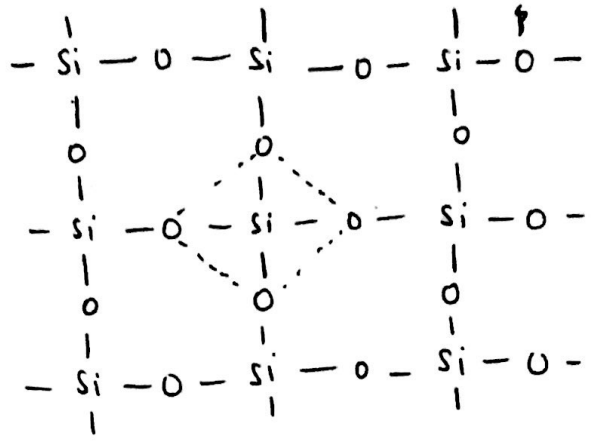
**$CO_2$**

$:\ddot{O}=C\overset{\curvearrowleft}{=}\ddot{O}: \longleftrightarrow :\ddot{O}=\overset{\ominus}{C}\equiv O^{\oplus}: \longleftrightarrow :O\equiv\overset{\oplus}{C}=\overset{\ominus}{\ddot{O}}:$

Most stable

(Structure with least formal charges is most stable)

## $SiO_2$



Hbd of Si = $sp^3$

C.N of Si = 4

C.N of O = 2

contribution of each O = $\frac{1}{2}$

In $SiO_2$, each Si is tetrahedrally surrounded by 4 oxygens

Each oxygen makes only $\frac{1}{2}$ contribution per tetrahedron. So its formula is $SiO_2$.

- $SiO_2$ is a giant 3-D polymer like ~~diamond~~ diamond.
- Si-O-Si bond in $SiO_2$ is not as strong as C-C bond in diamond. So diamond is harder than silica.
- Silica exhibits allotropy.

Molten Silica

Annealing (slow cooling) → Amorphous silica
Ex: Agate, Onyx, Jasper

Quenching (sudden cooling) → Crystalline silica
Ex: Quartz, Tridymite, Crystobalite

## 2. With water

- C, Si, Ge are not affected by water.

But in red-hot condition, they decompose steam.

$$\underset{\text{(Red hot)}}{C} + \underset{\text{(steam)}}{H_2O} \xrightarrow{>1000^\circ C} \underbrace{CO + H_2}_{\text{water gas}}$$

- Sn decomposes steam.

$$Sn + 2H_2O \text{ (steam)} \longrightarrow SnO_2 + 2H_2$$

- Pb ($E^\circ = -0.13\,V$) doesn't decompose water.

Reason: i) Presence of oxide film on its surface (Pb has mechanical passivity - as soon as it is formed, an oxide film is formed) makes it unreactive.

ii) Higher over-voltage is needed for the discharge of $H^+$ on the surface of Pb. So $H^+$ discharge is difficult.

## With hydrogen (Hydrides)

a) $C_nH_{2n+2}$, $C_nH_{2n}$, $C_nH_{2n-2}$

b) $Si_nH_{2n+2}$ ( n should not be greater than 8)

c) $Ge_nH_{2n+2}$ ( n should not be greater than 5)

d) $SnH_4$ - Stannane

$Sn_2H_6$ - Di stannane

e) $PbH_4$

Thermal stability : $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

$GeH_4 > SnH_4 > PbH_4$ → Thermally unstable due to weaker M-H bond

Reducing Power : $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$

- $SnH_4 + 4AgNO_3 \longrightarrow Sn + 4Ag + 4HNO_3$

$SnH_4 + 3H_2O \longrightarrow H_2SnO_3 + 4H_2$

$SnH_4 + 2Cl_2 \longrightarrow Sn + 4HCl$

** Thermal stability of Alkanes > Silanes

Reason: 1. EN difference

$$\overset{-\delta}{C}(2.5)\ —\ \overset{+\delta}{H}(2.1) \qquad \overset{+\delta}{Si}(1.8)\ —\ \overset{-\delta}{H}(2.1)$$

The positively charge Si is readily attacked by nucleophiles

2. Large size of Si makes Si-H bond weaker.

3. Presence of vacant 3d orbitals in Si

4. Halides:

Dihalides: ($MX_2$)

- C cannot form dihalides but halocarbenes are known.

Stability of halocarbenes : $:CF_2 > :CCl_2 > :CBr_2 > :CI_2$

Reason: $:CF_2$ is most stable due to effective back bonding from F to C (since C has sextet)

$$:C \overset{F}{\Longleftarrow} F$$

- Stability of dihalides : $SiX_2 < GeX_2 < SnX_2 < PbX_2$

Reason: Stability of +2 O.S increases

Tetrahalides ($MX_4$)

Stability : $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

Reason: Stability of +4 O.S decreases down the group.

- $PbBr_4$ and $PbI_4$ do not exist.

Reason: $Pb^{4+} + 4Br^- \longrightarrow PbBr_2 + Br_2$

$$Pb^{4+} + 4I^- \longrightarrow PbI_2 + I_2$$

1. $Pb^{4+}$ oxidises $Br^-$ and $I^-$ (It cannot oxidise $F^-$, $Cl^-$ as ~~they~~ they are powerful oxidising agent)

2. (Minor cause) – Larger size of $Br^-$ and $I^-$ cause steric crowding.

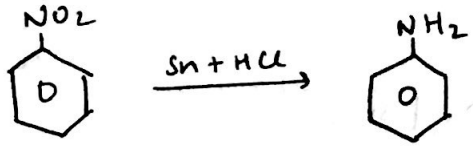
- Stability of $PbCl_2 > PbCl_4$

  $GeCl_2 < GeCl_4$

  $SnCl_2 < SnCl_4$

- $PbCl_4$ → good oxidant

  $SnCl_2$ → good reductant




$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

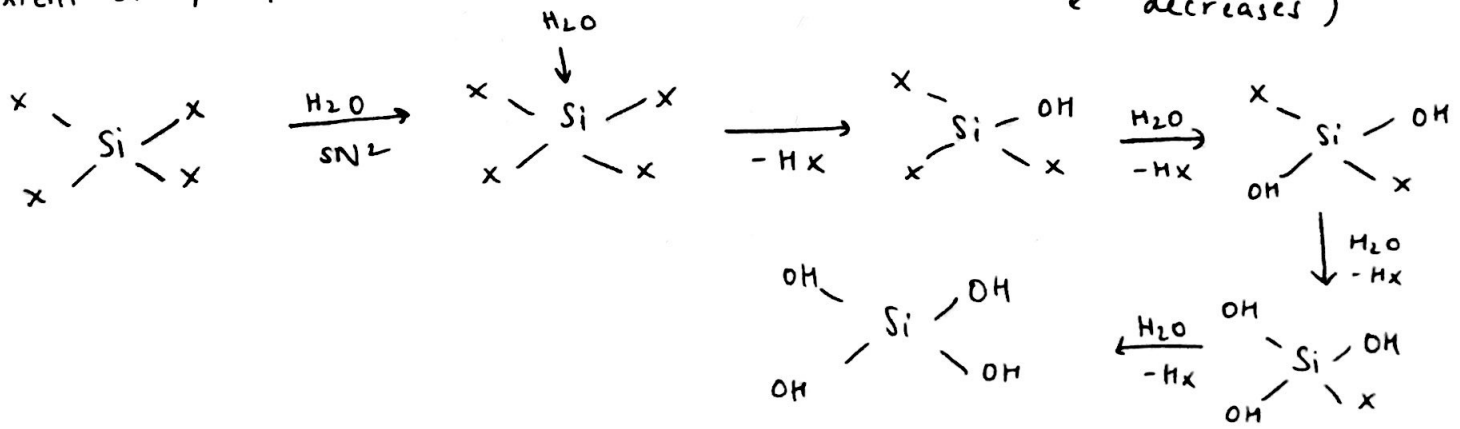
* $CX_4$ doesn't undergo hydrolysis nor acts as Lewis acid.

  Reason: Absence of d- orbitals.

- $SiX_4$, $GeX_4$, $SnX_4$, $PbX_4$ undergo hydrolysis and behave as Lewis acids.

  Lewis acidic nature: $SiX_4 > GeX_4 > SnX_4 > PbX_4$ (As size increases, the attraction towards incoming $e^-$ decreases)

  Extent of hydrolysis

- 


It follows $SN^2$ mechanism.

$$r = k[SiX_4][H_2O]$$

$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl$

$PbCl_4 + 2H_2O \rightleftharpoons PbO_2 + 4HCl$

$SnCl_4 \xrightarrow{\Delta} SnCl_2 + Cl_2$

$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

- $MX_4$ (M= Si, Ge, Sn, Pb) form complex halides

$MX_4 + 2X^- \longrightarrow [MX_6]^{2-}$

($MX_4$: (lewis acid); $2X^-$: (lewis base))

$M \rightarrow sp^3$ (Tetrahedral)

$M \rightarrow sp^3d^2$ octahedral

$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$

5. With alkalis:

- C is not affected by alkalis.

It reacts only with fused NaOH.

$C + 3NaOH \xrightarrow{\text{fused}} Na + Na_2CO_3 + \frac{3}{2}H_2$

- Si, Ge react slowly with dilute alkalis.

$2NaOH + Si + H_2O \longrightarrow Na_2SiO_3 + \frac{3}{2}H_2$

$2NaOH + Ge + H_2O \longrightarrow Na_2GeO_3 + \frac{3}{2}H_2$

$Sn + NaOH + H_2O \longrightarrow Na_2SnO_3 + \frac{3}{2}H_2$

Sodium stannate

$Pb + NaOH + H_2O \longrightarrow Na_2PbO_3 + \frac{3}{2}H_2$

Sodium plumbate

* $SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$

Sodium stannite

(or)

$Na_2[Sn(OH)_4]$

Similarly for Pb

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

Sodium stannate

Similarly for Pb

6. With acids:

- C, Si, ~~Ge~~ are not affected by dilute acids.

They are affected by conc. acids.

$C + HNO_3 \text{ (conc)} \longrightarrow CO_2 + NO_2 + H_2O$

$C + H_2SO_4 \text{ (conc)} \longrightarrow CO_2 + SO_2 + H_2O$

$Si + HNO_3 \text{ (conc)} \longrightarrow H_2SiO_3 + NO_2 + H_2O$

Meta silicic acid

- $Ge + 3HCl \text{ (dry)} \longrightarrow GeHCl_3 + H_2$

(Germanium chloroform)

- $Sn + 2HCl \text{ (dil)} \longrightarrow SnCl_2 + H_2$ (slow)

$Sn + 2HCl \text{ (conc)} \longrightarrow SnCl_2 + H_2$ (fast)

$Sn + H_2SO_4 \text{ (dil)} \longrightarrow SnSO_4 + H_2$

$Sn + H_2SO_4 \text{ (conc.)} \longrightarrow Sn(SO_4)_2 + SO_2 + H_2O$

$4Sn + 10HNO_3 \text{ (dil)} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

$Sn + 4HNO_3 \text{ (conc)} \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$

(meta stannic acid)

- i) $Pb + \underset{(dil)}{2HCl} \xrightarrow{slow} PbCl_2 + H_2$

* ii) $Pb + \underset{(conc)}{2HCl} \xrightarrow{PbCl_2} PbCl_2 + H_2 \longrightarrow PbCl_2 + 2HCl \longrightarrow H_2PbCl_4$
$\qquad\qquad\qquad

Refractive index = 2.45

MP = 3980°C

- Chemically inert
- Insoluble in any solvent

Bad conductor (No unpaired $e^-$)

- very hard due to strong C-C bonds
- $\Delta H^\circ_f = +1.9$ kJ/mol ($= \Delta G^\circ_f$ as $\Delta S$ is almost 0)

- Diamond has cubic lattice.

No. of C per unit cell of diamond = 8

- Diamond upon strong heating in air burns out as $CO_2$.

| 1 carat = 200 mg |
|---|

- Diamond dyes are used for:
  cutting glass, drilling rocks, drawing thin wires.

- Used as abrasive.
- Precious stone in jewellery
- Can diffract X-rays
- Glittery due to high TIR which arises due to higher $\mu$.
- Naturally occuring diamond - $N_2$ gas. Blue diamond - Al impurity

## 2. Graphite:

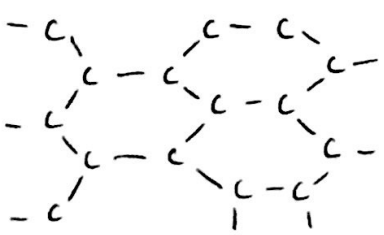
### Prep:

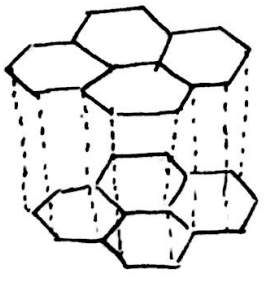
### Acheson's process:

$$SiO_2 + \underset{\substack{\text{(Anthracite)}\\ \text{Amp. allotrope}}}{3C} \xrightarrow{3000^\circ C} SiC + 2CO\uparrow$$

$$SiC \xrightarrow{\Delta} \underset{\text{(volatile)}}{Si\uparrow} + \underset{\text{(graphite)}}{C}$$

### Structure:





Diamagnetic

- Layer lattice structure

α- graphite : AB, AB, .... (hexagonal closed packing) hcp (1st and 3rd layer are same)

β - graphite : ABC, ABC, ... (ccp) (1st and 4th layers are identical)

Both are interconvertible

α- Graphite $\underset{\text{Heating}}{\overset{\text{Grinding}}{\rightleftharpoons}}$ β- Graphite

- $C \rightarrow sp^2$

  half filled unhybridized p-orbitals form π-bonds.

- C-C = 1.415 A° d = 2.22 g/cc

  $\hat{CCC}$ = 120° $\Delta H_f^\circ = 0 = \Delta G_f^\circ$ (Standard state of carbon (Thermodynamically most stable))

Layers are held by weak Vanderwaal's forces.
So they slip past each other.

- ∴ Graphite is soft and a lubricant. The lubricancy of graphite increases in the presence of air or $O_2$

Reason: The invading of $O_2$ molecules increases the distance between layers and decreases vanderwaal's forces.

Distance between successive layers of graphite = 3.35 A°

- Graphite is a good conductor of electricity.
  Reason- delocalization of π-electrons within the layer.
  * The conductivity is within the same layer but not between two different layers.

- Graphite leaves a black mark on paper. So it is called 'black lead' or 'plumbago'
- Lead pencil - Graphite + Clay
- Graphite is used for making refractory crucibles.

- Graphite is a neutral refractory material in metallurgy.
- Used as lubricant in industries.
- Used as electrodes.
- Used in nuclear reactors as control rod/moderator for absorbing neutrons.

$$\underset{\text{(graphite)}}{C} \xrightarrow[50000-60000\ atm]{1600^\circ C} \underset{\text{(Diamond)}}{C}$$

## Formation of Intercalation compounds

$$\text{Graphite} + \underset{\text{(vap.)}}{K/Rb/Cs} \xrightarrow{300^\circ C} C_8M$$

($C_8M$: Bronze colour due to metal cluster formation)

Intercalation compounds — Compounds formed due to the invading of atoms/molecules/ions between the layers of graphite.

These are non-stoichiometric.

- The occupation of atoms/ions/molecules increases the spacings between the layers without altering the delocalisation of π-electrons.

$$\text{Graphite} + \underset{(K,Rb,Cs)}{M} \xrightarrow{300^\circ C} \underset{\substack{\text{Bronze}\\(\text{metal clusters})}}{C_8M} \xrightarrow[-M]{350^\circ C} C_{24}M \longrightarrow C_{36}M \longrightarrow C_{48}M \longrightarrow C_{60}M$$

- Graphite → Diamagnetic
  Due to the invading of alkali metal ions ($M \rightarrow M^+ + e^-$) between the layers, additional electrons are added to the delocalized π-system which further increases the conductivity and makes the intercalation compound paramagnetic.

- Intercalation compounds are also formed by $F_2$, $Cl_2$, $Br_2$, HF, $CdCl_2$, $CuBr_2$, $FeCl_3$, $AlCl_3$, $ClF_3$, $TiF_4$, $MoCl_5$, $SbF_5$, $UCl_6$, $XeF_6$, $CrO_3$, $MoO_3$, $SO_3$, $N_2O_5$, $Cl_2O_7$, $FeS_2$, PdS, $V_2S_3$.

$C_{(graphite)} + F \longrightarrow CF_n$ $(n = 0.7 \text{ to } 0.98)$ layer distance increases to 8.1 Å

- Graphite $\xrightarrow[\text{(oxidising agents)}]{HNO_3 / HClO_4 / KMnO_4}$ Graphitic acid (or) Graphitic oxide (pale yellow lemon) $(C_{11}H_4O_5)$

  7 Å

  Unstable
  Non-stoichiometric
  * Non-conductor

Graphite oxide decomposes at 70°C. Emp. formula = $C_{11}H_4O_5$

At 200°C, it catches fire and produces C, CO, $CO_2$ & $H_2O$.

- In graphitic oxide, the $C_6$ units are in chair form with few double bonds. These double bonds form oxygen bridges (C–O–C) & C=C–OH.

  C=C–OH is converted to $-CH-\overset{\overset{O}{\|}}{C}-$

  $-\overset{|}{C}=C-O-H \rightleftharpoons -CH-\overset{\overset{O}{\|}}{C}-$ (Enolization)

  some carbons

Because of this, all the 4 $e^-$ of carbons are utilized for forming $\sigma$ bonds only which destroys the delocalized $\pi$-$e^-$ system.

∴ The conductivity ~~diminishes~~ is inhibited.

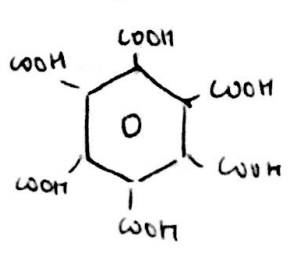
The Oxygen bridges buckle up the layers.

- Graphitic oxide absorbs molecules such as $H_2O$, $C_2H_5OH$, $CH_3COCH_3$ etc

  Reason- These molecules invade in between the layers.

  8 Å

- Graphite $\xrightarrow[\Delta]{\text{alk. } KMnO_4}$ Mellitic acid (yellow) + Oxalic acid



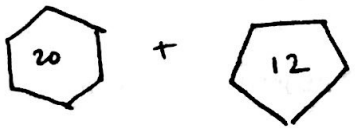

$\rightarrow C_6(COOH)_6$

COOH
|
COOH

Graphite $\xrightarrow[\Delta]{H_2CrO_4}$ $CO_2$

Graphite $\xrightarrow{\text{dil. acids}}$ No reaction

## Buckminister Fullerene ($C_{60}$)

- It is the purest form of Carbon without danglings bonds.
- It is a cage-like molecule.
- 

→ 60 vertices
- Hexagonal ring fuses with both hexagonal and pentagonal rings. Pentagonal rings fuse only with hexagonal rings.
- C → $sp^2$ hbd
  The unpaired $e^-$ at each Carbon delocalize in the molecular orbitals imparting aromatic nature.
- C – C ⟶ 142.5 pm
  C = C → 138.3 pm
- Density = 1.5 g/cc
- $\Delta H^\circ_f = \Delta G^\circ_f$ = 38.1 kJ/mol (Thermodynamic stability : Graphite > Diamond > $C_{60}$)
- It is readily soluble in non-polar solvents like hexane, benzene, toulene.
  $C_{60}$ in Toulene → Purple solution
  $C_{70}$ in Toulene → Red
- $C_{60} + K \longrightarrow KC_{60}$ (superconductor below 18 K)
  $C_{60} + 3Rb \rightarrow Rb_3C_{60}$ (superconductor below 28 K)

- $C_{60} + 5F_2 \longrightarrow C_{60}F_{10}$

Prep:

1. Subjecting graphite to intense laser beam to heat to a temp. 10,000°C gives $C_{60}$.

2. Graphite is heated in an electric arc.
The vapours thus produced upon condensation produces a sooty deposit which mainly consists of $C_{60}$, some amount of $C_{70}$ and traces of other fullerenes having Carbons upto or above 370.

## Amorphous allotropes

1. Coal:

It is obtained the slow decomposition of vegetable matter under pressure, heat in limited supply of air.

| | |
|---|---|
| Peat | 60% C |
| Lignite | 67% C |
| Bituminous | 88% C |
| Anthracite | 95% C |

- Anthracite is the purest form of Coal which burns with non-smoky flame.
- Bituminous is common variety of coal which burns with smokey flame.

Coal $\xrightarrow[\text{Distillation}]{\text{Destructive}}$ Coal gas + Coke + Coal Tar + Ammonical liquor

Coal Tar $\xrightarrow{\text{Fractional dist}}$ Petroleum Products

2. Coke:

It is obtained by destructive distillation of coal.

- It burns with non smokey flame.

- It is used as :
  i) Reducing agent
  ii) Used for production of fuel gases
  iii) Preparation of graphite

3. Charcoal:

Charcoal is obtained by the slow decomposition of wood / cellulae or other carbonatious materials in limited supply of air.

Ex: Wood charcoal, Sugar charcoal, Animal charcoal, Coconut charcoal

- Sugar charcoal is the purest form of charcoal.
- Activated charcoal is obtained by heating the charcoal to 700° to 800° C in a current of steam.

Uses:

i) Animal charcoal is used for adsorbing colouring matter from raw sugar syrup in sugar industry.
ii) Activated charcoal is used for adsorbing poisonous gases and for removing offensive odours.
iii) Activated ~~car~~ charcoal is used for purifying water.
iv) Activated coconut charcoal is used for separating noble gases in Diwar's method
v) Activated carbon is used in gas masks.
vi) Acetic acid is adsorbed from its aqueous solution by using activated charcoal.

4. Lamp black / Gas Carbon / Petroleum Coke :

It is the soot deposited on wet blankets when petrol / diesel / turpentine oil / acetylene or any other carbon rich compounds are burnt in limited supply of air.

- $C_{60} + SF_2 \longrightarrow C_{60}F_{10}$

Uses:

- Indian ink
- Printing ink
- Filler in tires

## Fuel gases:

1. **Water gas**: $CO\ (40\text{-}50\%) + H_2\ (45\text{-}50\%) + \text{Traces of } CO_2, N_2$

$$\underset{\text{(Red hot coke)}}{C} + \underset{\text{(Steam)}}{H_2O} \xrightarrow{>1000^\circ C} \underset{\text{water gas}}{(CO + H_2)} \quad ; \quad \Delta H = +28\ kcal$$

- Water gas burns with blue flame ( CO - blue flame, $H_2$ - colourless flame)
  ∴ It is called blue gas
- The above reaction is endothermic. So the temp. of coke bed falls.
  To maintain the temp. of coke bed, hot air is admitted.

$$C + O_2 \longrightarrow CO_2 \quad ; \quad \Delta H = -97.7\ kcal$$

(overall process is exothermic)

- Caloritic value : 310 B·Th·U / $ft^3$ (British Thermal Units)

1 B·Th U = 1055 J

- Blue flame.
  ∴ It is called blue gas
- Many chemicals are synthesized from water gas. So it is called 'Syn-gas' or 'Synthesis gas'.

Uses:

i) Fuel in steel, ~~glass~~ industries.

ii) Synthesis of $H_2$. (water gas is the main source of $H_2$)

iii) Manufacture of $NH_3$

2. **Producer gas** : CO (25%) + $N_2$ (70%) + 4% ($CO_2$) + Traces of $H_2$

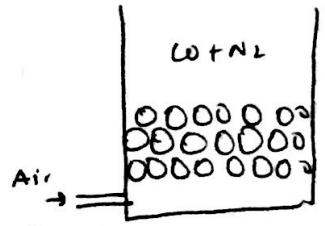
$$C \text{ (Red)} + O_2 \text{ (Air)} \longrightarrow CO_2 \qquad \Delta H = -97.7 \text{ kcal/mol}$$

$$CO_2 + C \longrightarrow 2CO \qquad \Delta H = +38.1 \text{ kcal/mol}$$

$$2C + O_2 \longrightarrow 2CO \quad ; \quad \Delta H = -59.6 \text{ kcal}$$

(keeps the gas in hot condition)

- Calorific value - 103 B.Th.U/$ft^3$
- Should be used on spot - 'spot gas' while in hot condition.




As $CO_2$ rises up, it gets reduced to CO. $N_2$ from air is left as it is inert.

Uses:

- Manufacture of $N_2$
- Used in gas generator
- Fuel in steel, glass industries

3. **Coal gas**

CO (10.9%) $H_2$ (56%) $N_2$ (5%) $CH_4$ (22.8%)

$CO_2$ (1.3%) Ethylene + Acetylene (2.5%)

- Calorific value = 450 - 650 B.Th.U/$ft^3$

1 B.Th.U = 1055 J

- It is an illuminating gas.

4. **Carburetted water gas** : Water gas + Saturated, Unsaturated Hydrocarbons

Calorific value of water is improved by adding HC

5. **Semi water gas**: CO + $H_2$ + $N_2$

It is obtained by passing a mixture of air & steam over heated hot coke.

- Natural gas mainly contains methane (85%)

- LPG - Propane + Butane + Isobutane + Butene + Mercaptane ($C_2H_5SH$)
  ↓
  odour for detecting leakage.

## Carbon:

- $C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.5\ kJ\ mol^{-1}$

- Good reducing agent.

$$C + ZnO \longrightarrow Zn + CO$$

$$C + PbO \rightarrow Pb + CO$$

$$Fe_2O_3 + C \longrightarrow Fe + CO$$

- $C + CaSO_4 \longrightarrow CaS + CO$

$$C + BaSO_4 \longrightarrow BaS + CO$$

- $\underset{(Red)}{C} + \underset{(steam)}{H_2O} \longrightarrow CO + H_2$

$$\underset{(Red)}{C} + \underset{(vap)}{2S} \longrightarrow CS_2$$

- Acetylene is obtained by striking graphite electrodes in the atmosphere of $H_2$.

$$2C + H_2 \longrightarrow C_2H_2$$

- $2Be + C \xrightarrow{\Delta} Be_2C$

$$Al_2O_3 + C \longrightarrow Al_4C_3 + CO$$

$$CaO + C \longrightarrow CaC_2 + CO$$

$$SiO_2 + C \longrightarrow SiC + CO$$

- $C + \underset{(conc)}{HNO_3} \longrightarrow CO_2 + NO_2 + H_2O$

$$\underset{(graphite)}{C} + \underset{(hot\ dil)}{HNO_3} \longrightarrow \text{Artificial tannin}$$

Artificial tannin is used to stabilize colloidal sols.

- $C + H_2SO_4 \longrightarrow CO_2 + H_2O + SO_2$ - Major reaction

$C + H_2SO_4 \longrightarrow C_6(COOH)_6 + SO_2 + H_2O$ - Minor
(Trace)

## CO

- Colourless gas
- Slightly soluble in water.

## Prep:

1. $H_2C_2O_4$ (or) $\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} CO + CO_2$

Oxalic acid

2. $HCOOH \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} CO$

Formic acid

3. $Zn + CO_2 \xrightarrow{\Delta} ZnO + CO$

$MgCO_3 + Zn \longrightarrow MgO + ZnO + CO$

4. $Fe_2O_3 + C \longrightarrow Fe + CO$

$ZnO + C \longrightarrow Zn + CO$

****
5. $K_4[Fe(CN)_6] + 3H_2SO_4 \text{ (dil)} \longrightarrow 2K_2SO_4 + FeSO_4 + \boxed{6HCN}\uparrow$ (poisonous gas)

$K_4[Fe(CN)_6] + 6H_2SO_4 \text{ (conc)} + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6\boxed{CO}\uparrow$

6. $\underset{(g)}{CO_2} + \underset{(s)}{C} \longrightarrow \underset{(g)}{2CO}$

- CO is combustible and burns with blue flame.

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$ $\quad \Delta H = -ve \quad \Delta G = -ve \quad \Delta S = -ve$

- CO → good reductant.

$$CO + Fe_2O_3 \longrightarrow 2Fe + 2CO_2$$

$$PbO + CO \longrightarrow Pb + CO_2$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

- CO reduces Fehling's reagent ($Cu^{+2}$ ion + Tartarate)

$$CO + Cu(OH)_2 \longrightarrow \underset{\text{(Red ppt)}}{Cu_2O} \downarrow + CO_2 + H_2O$$

- Estimation of $O_2$ using $I_2O_5$.

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

- $(CO + H_2) + H_2 \xrightarrow{ZnO + Cr_2O_3} CH_3OH$

- $CO + S \xrightarrow{\Delta} COS$

- $CO + Cl_2 \xrightarrow{h\upsilon} COCl_2$ (phosgene - poisonous gas)

- $(CO + H_2) + H_2 \xrightarrow{Rh\ (Rhodium)}$ Gasoline

- $CO + CuCl \longrightarrow CuCl \cdot CO$

CO is absorbed by ammonical cuprous chloride (CuCl)

Hydro formation:

- $CO + \underset{\text{(Alkene)}}{R-CH=CH_2} + H_2 \xrightarrow[\Delta]{\text{high P}} \underset{\text{(Aldehyde)}}{R-CH_2-CH_2-CHO}$

- $CO + NaOH \xrightarrow{\text{high P}} \underset{\text{(Sodium formate)}}{HCOONa}$

- CO is a poisonous gas as it forms carboxy haemoglobin complex which is 300 times stronger than oxyhaemoglobin - (causes asphyxia)

- CO poisoned victims are treated with Carbogen.

  Carbogen - $CO_2$ (5-10 %) + $O_2$ (90-95 %)

- CO forms stable metal carbonyls.

  $Ni + 4CO \longrightarrow Ni(CO)_4$

  The above reaction helps in the purification of Ni by Mond's process

  $Fe + 5CO \longrightarrow Fe(CO)_5$

- CO is a good reductant. It is used for the extraction of metals.

## $CO_2$

$CaCO_3 \longrightarrow CaO + CO_2$

$Ag_2CO_3 \longrightarrow 2Ag \downarrow + CO_2 \uparrow + \frac{1}{2}O_2 \uparrow$

- Fermentation: $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

- $CO_3^{2-}$ / $HCO_3^{2-a}$ + Dil acids $\rightarrow CO_2$

  $HCO_3^- \xrightarrow{\Delta} CO_3^{2-} + CO_2 + H_2O$

- Mg, Na continue to burn in $CO_2$ atmosphere due to high heat of reaction.

  $2Mg + CO_2 \longrightarrow 2MgO + C$

  $4Na + CO_2 \longrightarrow 2Na_2O + C$

- $CO_2 + 2NH_3 \xrightarrow[\text{High P}]{180^\circ C} CO(NH_2)_2 + H_2O$ (urea)

- $K_2O + CO_2 \longrightarrow K_2CO_3$

  $Na_2O + CO_2 \longrightarrow Na_2CO_3$

- $CS_2 + 2NH_3 \longrightarrow CS(NH_2)_2 + H_2S$ (thio urea)

- Photosynthesis: Zero order as it is a photochemical reaction.

  $6CO_2 + 6H_2O \xrightarrow{h\nu} \overset{C_6H_{12}O_6}{C_{12}H_{22}O_{11}} + 6O_2$

- $CO_2$ → neither combustile nor supporter of combustion.

  So it is used for extinguishing fires.

Soda-acid type : $NaHCO_3 + H_2SO_4$ (Conc)

Foam type : $NaHCO_3 + Al_2(SO_4)_3$

$$NaHCO_3 + Al_2(SO_4)_3 \longrightarrow 2Al(OH)_3$$

gelatinous (prevents fire)

$$Al_2(SO_4)_3 + H_2O \longrightarrow Al(OH)_3$$

## Carbon Suboxide ($C_3O_2$)

$$O = \underset{+2}{C} = \underset{0}{C} = \underset{+2}{C} = O \qquad \text{Avg. O.S} = 4/3$$

Anhydride of malonic acid.

Prep:

$$CH_2(COOH)_2 \xrightarrow{P_4O_{10}} C_3O_2 + 2H_2O$$

Malonic acid

- $CH_2(COOH)_2 + 2NH_3 \longrightarrow CH_2(CONH_2)_2 + H_2O$

- $CH_2(COOH)_2 + HCl \longrightarrow CH_2(COCl)_2 + H_2O$

  $CH_2(COCl)_2 \xrightarrow{H_2O} CH_2(COOH)_2$

Types of Carbides : ~~Carbides are formed by IA, IIA, IIIA (except B), Zn, Cd, Cu, Ag, Au and few lanthanides~~

1. Ionic carbides – IA, IIA, IIIA (except B), Zn, Cd, Cu, Ag, Au, few lanthanides

a) Acetylides ($C_2^{2-}$)

- $M_2C_2$ (M = IA, Cu, Ag, Au)

$$Na_2C_2 + 2H_2O \longrightarrow C_2H_2 + 2NaOH$$

$$CuC_2 + 2HCl \longrightarrow C_2H_2 + Cu_2Cl_2$$

- $MC_2$ (M = IIA, Zn, Cd) → NaCl like structure

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

b) Methanides ($C_4^{4-}$)

$Al_4C_3$, $Be_2C$, $Mn_3C$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

c) Allylides ($C_3^{4-}$)

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C\equiv CH$$

2. Covalent carbides (Network carbides)

SiC, $B_4C$

$$SiO_2 + C \xrightarrow{2500^\circ C} SiC + CO$$

- SiC - Carborundum - Used as abrasive

Diamond like structure

Very hard

Chemically inert

SiC is insoluble in solvents but dissolves in NaOH.

$$SiC + NaOH + O_2 \longrightarrow Na_2SiO_3 + Na_2CO_3 + H_2O$$

$$SiC + 2Cl_2 \xrightarrow{\Delta} SiCl_4 + CCl_4$$

- $B_4C$ - used as shield for radioactive /nuclear radiations.

3. Interstitial Carbides (Non - stoichiometric)

- Same lustre as metal
- Good conductors
- ~~Very hard~~ Extremely hard
- Chemically inert.

- MC Type ( Ti, Zr, Hf, V, Nb, Ta, W, Mo)
- $M_2C$ type ( V, W, Mo)
- WC (Tungsten carbide) is used for making high speed tools.

## Carbonates

- $Na_2CO_3$ is used for removing hardness of water.

$$MgCl_2 / MgSO_4 / CaCl_2 / CaSO_4 + Na_2CO_3 \longrightarrow \underset{\text{Ppt}}{MCO_3 \downarrow}$$

- $2NaHCO_3 + MgSO_4 \longrightarrow Mg(HCO_3)_2 + Na_2SO_4$

$$\downarrow \Delta$$

$$MgCO_3 \downarrow + CO_2 \uparrow + H_2O$$

- $Na_2CO_3 + SiO_2 \longrightarrow \underset{\text{(water glass)}}{Na_2SiO_3}$

## Silicon

- Amorphous & Crystalline - Amp is more reactive

$$SiO_2 + 2Mg \longrightarrow \underset{\text{(Amp)}}{Si} + 2MgO$$

$$SiO_2 + 2C \longrightarrow \underset{\text{(Cryst)}}{Si} + 2CO$$

$SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$
(pure)

$SiCl_4 \xrightarrow{LiAlH_4} SiH_4 \xrightarrow{\Delta} Si$
(Ultrapure Si)

- Si is refined by zone refining method

- $Si + 2H_2O \longrightarrow SiO_2 + 2H_2$

$Si + 4KOH \longrightarrow K_4SiO_4 + 2H_2$

$Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$

$Si + Na_2CO_3 \longrightarrow Na_2SiO_3 + C$

$Si + 2Mg \longrightarrow Mg_2Si$
Mg silicyte (Alloy)

- $Si + O_2 \longrightarrow SiO_2$
(Silica)

Crystalline form of $SiO_2$ - Quartz.

α-Quartz is stable at room temp.

- Crushed form of silica - Sand
- Kiesulguhs is a silicious rock containing sea insects. It acts as good adsorbent.
- $SiO_2$ is insoluble in all acids except **HF**

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

$SiF_4 + H_2O \longrightarrow Si(OH)_4$ (or) $H_4SiO_4$
Ortho silicic acid

$Si(OH)_4 \xrightarrow[-H_2O]{1000^\circ C} H_2SiO_3$
Meta silicic acid

- HF is used for glass etching (as HF reacts with silica)

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

- $SiO_2$ when treated with dilute HCl produces silica gel, which is a very good adsorbent in column chromatography (either silica gel or alumina is used for column chromatography)

  Silica gel - $SiO_2 \cdot xH_2O$

- $$Na_2SiO_3 + H_2O \rightleftharpoons H_2SiO_3 + 2NaOH$$

## Organo silicones

These are organo silicon compounds containing Si-O-Si & Si-C bonds

Alkyl chloro silanes $\xrightarrow{H_2O}$ Alkyl silanols $\xrightarrow[\text{Polymerization}]{\text{condensation}}$ Organo silicones

Step: 1 Formation of chloro silanes

$$RMgCl + SiCl_4 \longrightarrow \underset{\text{Alkyl chloro silane}}{RSiCl_3} + MgCl_2$$

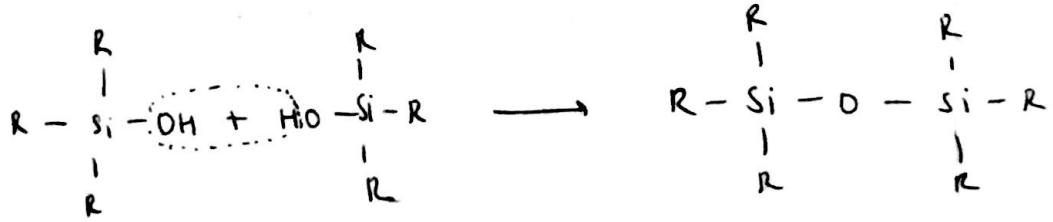
$$2RMgCl + SiCl_4 \longrightarrow \underset{\text{Dialkyl chloro silane}}{R_2SiCl_2} + 2MgCl_2$$

$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

- $$RCl + Si \xrightarrow[300^\circ C]{Cu} R_2SiCl_2$$

Step: 2 Hydrolysis followed by polymerization

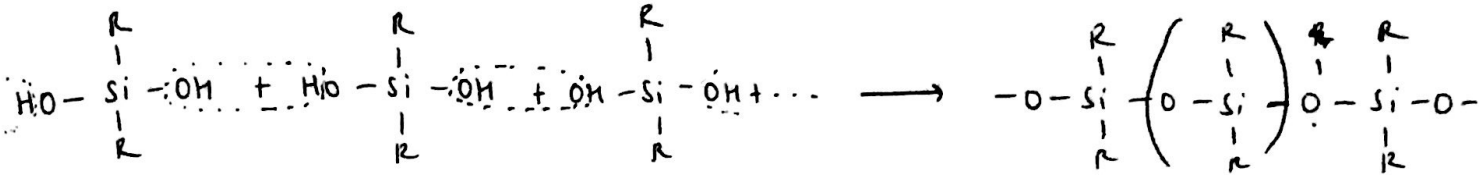
a) $R_3SiCl \xrightarrow{H_2O} R_3Si(OH) \xrightarrow{\text{polymerization}}$ Disilicone



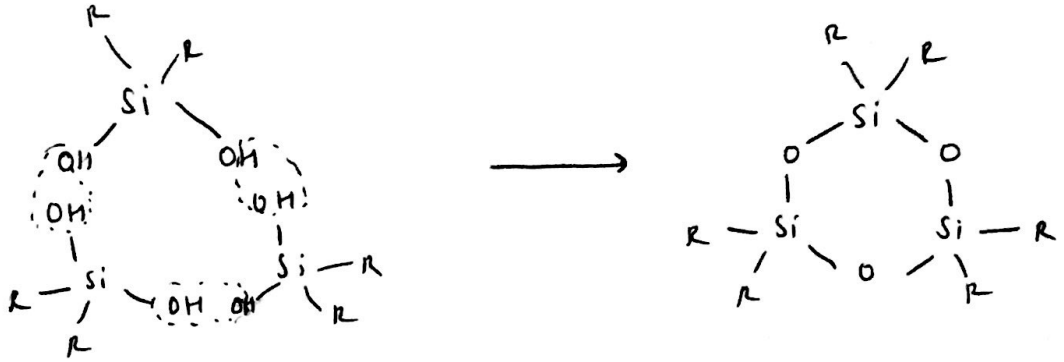
- $R_3SiCl$ or $R_3SiOH$ is used for terminating the length of silicone chain

b) $R_2SiCl_2 \xrightarrow{H_2O}$ $R_2Si(OH)_2$ (Dialkyl silanol) $\xrightarrow{\text{polymer}}$ Linear silicone / Cyclic silicone

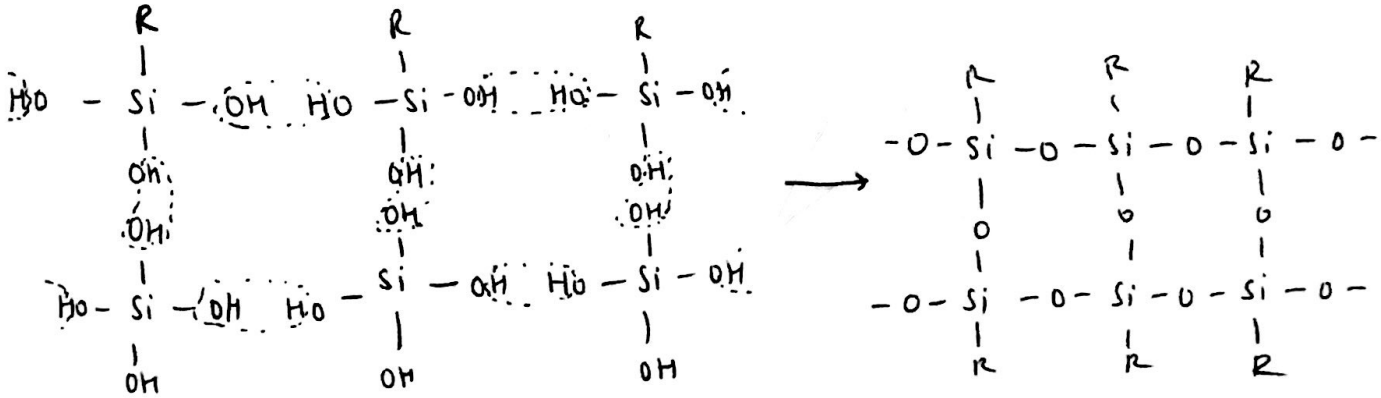
Linear silicone:



Cyclic silicone:



c) $RSiCl_3 \xrightarrow{H_2O}$ $RSi(OH)_3 \xrightarrow{\text{Polymerisation}}$ Cross linked polymer



## Properties of Silicones

Chemically inert and are resistant to sunlight and high temperatures.

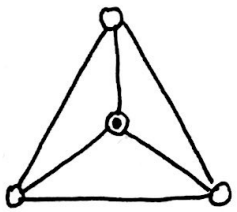
∴ They are used for paints and enamels.

- Resistant to water. ∴ Are used to make waterproof cloth & paper.
- Electrical insulators. Hence are used as insulating materials for electric motors and other electric appliances.
- These are non-toxic.
- Viscosity of silicone oils remains the same at different temp. and hence are used as lubricants in aeroplanes.
- Used for making vaseline.
- Silicone rubbers retain their elasticity over a range of temperature.
- Silicone oils are used for high temp. oil bath, high vaccuum pumps and low temp. lubrication.

## Types of Silicates

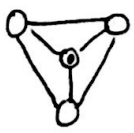
$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{ortho silicic acid}}{H_4SiO_4} + 4HCl$$

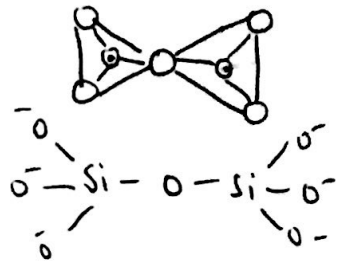
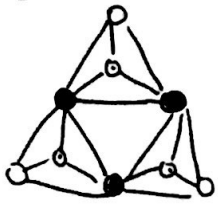
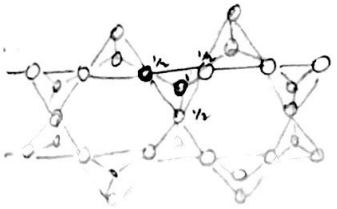
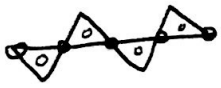
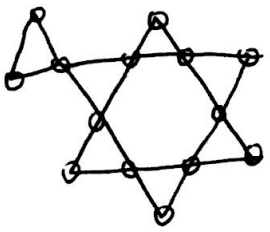
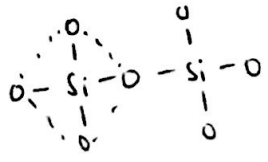
Silicates are the metal salts of $H_4SiO_4$. They consist of $SiO_4^{4-}$ tetrahedra.



- Si
- O

$SiO_4^{4-}$ Tetrahedron

| Name of silicates | Formula | No. of Oxygen atoms per tetrahedron | Examples |
|---|---|---|---|
| Ortho (or) Neso silicates | $SiO_4^{4-}$ (discrete)  | 0 | • Zircon - $ZrSiO_4$<br>• Willenite - $Zn_2SiO_4$<br>• Phenacite - $Be_2SiO_4$<br>• Forsterite - $Mg_2SiO_4$ (Olivine) |

| Name of silicate | Formula | No. of oxygen shared per tetrahedron | Examples |
|---|---|---|---|
| Pyro (or) Soro (or) di silicates (Island silicates) | $Si_2O_7^{6-}$  | 1 | ~~• Scot~~<br>• Thortvetite $- Sc_2Si_2O_7$<br>• Hemimorphite $- Zn_3Si_2O_7 \cdot Zn(OH)_2 \cdot H_2O$ |
| Cyclic silicates | $(SiO_3)_n^{2n-}$  | 2 | • Beryl $- Be_3Al_2Si_6O_{18}$<br>• Benitoite $- BaTiSi_3O_9$<br>• Wallastonite $- Ca_3Si_3O_9$<br>• Catapleite $- Na_2ZrSi_3O_9 \cdot 2H_2O$ |
| Chain silicates  | Pyroxenes → $(SiO_3)_n^{2n-}$ (single stranded)  <br>Amphiboles → $(Si_4O_{11})_n^{6n-}$ (Double stranded) | 2<br>2.5 | • Spodumene $LiAl(SiO_3)_2$<br>• Jadeite $NaAl(SiO_3)_2$<br>• Enstatite $- MgSiO_3$<br>• Diopside $- CaMg(SiO_3)_2$<br>• Tremolite $- Ca_2Mg_5(Si_4O_{11})_2(OH)_2$<br>• Asbestos $- CaMg_3(SiO_3)_4$ |
| 2-D sheet silicates | $(Si_2O_5)_n^{2n-}$  | 3 | • Talc $- Mg(Si_2O_5)_2 Mg(OH)_2$<br>• Kaoline $- Al_2(OH)_4Si_2O_5$<br>Zeolite:<br>Permutit $- Na_2Al_2SiO_8 \cdot xH_2O$<br>→ Sodalite $- Na_8[Al(SiO_4)_6]Cl_2$<br>→ Nosean $- Na_8[Al(SiO_4)_6]SO_4$<br>Ultramarine $-$ Ultramarine $(Na_8(AlSiO_4)S_2]^{\cdot}$ |
| 3-D Silicates<br>Network / Frame work silicates | $SiO_2$  | 4 | Quartz<br>Tridemite<br>Cristobalite<br>Feldspars: Orthoclase ($KAlSi_3O_8$)<br>Celsian ($BaAl_2Si_2O_8$) |